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SOME COMPOUNDS OF BORON, OXYGEN, AND HYDROGEN

SOME time ago, two of us communicated to the Royal Society (*Proc. Roy. Soc.*, A, **87**, 163) a preliminary account of certain compounds of boron, which had been obtained in solution by treating magnesium boride with water. The experiments which we had carried out pointed to the existence of a new group of compounds, possessing very remarkable properties; and though the results were in many respects inconclusive, we decided to publish them, mainly for the reason that some time must elapse before it would be possible to proceed further with the work.

About a year after the first publication the investigation was taken up again, and both the reaction between magnesium boride and water, and the substances in the resulting solution, were more fully studied. It was then found that for a variety of reasons, which will become apparent in the course of the paper, many of our earlier deductions required to be corrected. It may be pointed out that the substances which we were investigating were not only very unstable, but it was quite impossible to separate them from their solutions or to purify them in any way. It was therefore very important to guard against being misled by constant errors, due to experiments having been carried out under identical conditions, and in order to eliminate such errors we carried out a very large number of experiments, varying the conditions as much as possible. However, to publish the numerical results of all these experiments would serve no useful purpose, so in the following paper we have, as a rule, set down only the results of a few experiments, stating, where it is necessary, that they have been duly confirmed.

The prosecution of a research of this kind requires not only patience, but also time, which none of us are likely to have at

our disposal in the near future. We hope, however, that others will take up the work, and we have therefore decided to publish our results in the present form, in which we are not limited either in matters of detail or in regard to our speculations as to the constitution of the boron compounds.

We have divided the paper into three parts:

Part I.: The reaction between magnesium boride and water, analytical methods, etc.

Part II.: The products of the reaction between magnesium boride and water, boron compounds with two boron atoms in the molecule.

Part III.: The reaction between the boride, after treatment with water, and strong ammonia, and the products of this reaction, compounds having four boron atoms in the molecule.

PART I

Magnesium Boride

Moissan (*C.R.*, **114**, 392) and Winckler (*Ber.*, **23**, 772) have stated that borides of magnesium other than the compound B_2Mg_3 exist, and in our preliminary communication we suggested that the borohydrates might be formed by the action of water on some such compounds. This view was supported by certain of our experiments, from the results of which it appeared that a relationship existed between the hydrogen evolved when the crude boride was treated with water, and the borohydrate formed in solution. Further experiments showed, however, that the close agreement between the results of the first series was due to the fact that they had been carried out under almost identical conditions, and that by varying the conditions totally different results were obtained. A series of experiments were then carried out with a view to investigating the relationship between the composition of the mixture from which the crude boride was prepared, the temperature to which the mixture was heated, and the nature of the solutions obtained by treating the product with water. The results of these experiments led to the conclusion that, when a mixture of $2\frac{1}{4}$ parts of magnesium powder and 1 part of anhydrous boric acid is heated in a covered crucible in a current of hydrogen, sufficiently strongly to render the reaction complete, the solution obtained by treating the product with water is free from boric acid and from magnesium borate, and contains only the substances which we have called borohydrates. It is necessary that the boric acid should be perfectly anhydrous and finely powdered, and it was generally found that unless the mixture had deflagrated gently while it was being heated the reaction was not quite complete. We shall refer to solutions prepared from the crude boride obtained in this manner as

belonging to " Class A." If, on the other hand, the mixture contains excess of boric acid, or is insufficiently heated, the resulting solution, which we shall refer to as of " Class B ", contains both magnesium borate and boric acid, together with a borohydrate which appears to be one of the constituents of the solutions of Class A. However, since solutions of Class B can be obtained by the action of water on the boride to which a little boric acid has been added, and which would otherwise yield only a solution of Class A, there is no reason to suppose that the solutions of Class B are produced by the action of water on any compound other than the boride B_2Mg_3.

Since our preliminary communication was published, Mr. R. C. Ray has carried out an investigation on the composition of magnesium boride, and from the results of his experiments it would appear that it corresponds to the formula B_2Mg_3, and that no other boride is formed (*Chem. Soc. Trans.*, 1914, **105**, 2162).

The Action of Water on Magnesium Boride.

On addition of water to the crude boride the mixture becomes very hot, hydrogen is evolved—rapidly at first, and afterwards more slowly—and borohydrates appear in the solution. As Stock and his collaborators have shown, the hydrogen contains traces of volatile hydroborons, which impart to it a peculiar odour. In preparing the borohydrate solutions, we usually mixed 50 grams of the powdered boride with 150 grams of crushed ice in a flask from which the air was removed by means of hydrogen, and which was cooled in an ice-bath. After standing for twenty-four hours the solution was filtered off, and a further quantity of about 100 c.c. of water was added to the boride in the flask. After a further period of twenty-four hours a fresh quantity of the solution could be drawn off, and it was these second and third extracts which were usually taken for analysis. Sometimes the boride could be treated with water four or five times, but after a time the solutions became too weak to be of use.

In certain of our experiments the hydrogen which was given off was collected, and the product of the action of water on the boride was analyzed. The following are the results obtained in one complete series of experiments:

Action of Water on Magnesium Boride.

Quantity of boride taken: 80 grams.
Water changed seven times.
Boron as soluble borohydrate: about 0·6 gram.

Time in Hours.	*Volume of Hydrogen in c.c. at 0° and 760 mm.*
2	2,850
17	3,850
41	5,100
65	7,920
89	10,400
113	12,080
137	13,080
189	15,000
258	15,260
303	15,350
413	16,600

When the rate of evolution of the hydrogen fell to less than 100 c.c. in the twenty-four hours the experiment was brought to an end. The total quantity of hydrogen evolved down to this point may be expressed as 0·0187 gram of hydrogen per gram of the original crude boride, one gram of which on analysis was found to consist of—

Magnesium	0·6773
Boron as boride, soluble in dilute acid ..	0·0718
Residue insoluble in dilute acid (free boron, etc.)	0·0209
Oxygen (difference)	0·2300

The total quantity of boron in one gram of the crude boride is 0·0927 gram, which does not differ materially from the quantity calculated from the boric acid in the mixture from which it was prepared, which is 0·096 gram.

That the boron in the crude boride which dissolves in dilute acids is present as a boride of the form B_2Mg_3 is proved by the fact that, while a gram of it, when dissolved in acid, yielded 0·0388 of hydrogen, one gram of a substance containing 0·0718 of boron as the boride B_2Mg_3 should yield 0·0391 gram of hydrogen according to the equation

$$B_2Mg_3 + 6HCl = 3MgCl_2 + 2B(OH)_3 + 6H_2.$$

It will now be observed that the reaction between water and the crude boride gives rise, for each gram of the boride, to 0·0187 gram of hydrogen, which is only very slightly less than one half the quantity evolved by the action of acid. That it is less is due to the fact that the reaction between water and the boride comes to an end only very slowly. The reaction between the boride and water may, then, be represented by the equation

$$B_2Mg_3 + 6H_2O = Mg_3B_2(OH)_6 + 3H_2.$$

The product of this reaction, which is completely insoluble in water, may be regarded as a borohydrate of the formula $B_m(OH_2)_n$ combined with the elements of magnesium oxide.

The properties of this compound will be considered later in the paper (Part III.).

In order to confirm these results, a quantity of the "spent boride", produced by the action of water on the crude boride, was dried *in vacuo* and analyzed. Using 1 gram of the product, the following results were obtained:

Boron soluble in dilute acid	0·0280
Hydrogen evolved by dilute acid	0·0077

If the boron soluble in dilute acid were present as the insoluble compound $Mg_3B_2(OH)_6$, 1 gram of the product should yield 0·00765 gram of hydrogen.

So far as the first part of this investigation is concerned, the importance of these experiments lies in the fact that the reaction between magnesium boride and water does not, as has generally been supposed, result in the formation of magnesium borate or boric acid. Neither of these substances appears to be produced in any appreciable quantity, and they need not be considered as probable impurities in the borohydrate solutions. The magnesium derivative to which we have given the formula $Mg_3B_2(OH)_6$ also appears to be completely insoluble in and inactive towards both hot and cold water.

Magnesium Metaborate.

In the course of this research we found it necessary to investigate the properties of magnesium metaborate, and the details of this work, which was carried out by Mr. N. M. Gupta, will be

published separately. It is sufficient for the present to state that, when a solution of boric acid is shaken with " light " magnesia, a solution is formed which, on analysis, is found to contain boric acid and magnesia almost exactly in the proportions represented by the formula $Mg(BO_2)_2$. The values obtained for the depression of the freezing-point and the electrical conductivities of the solutions indicate that the ionization of the salt is of the same order as that of magnesium sulphate (Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 487).

Methods of Analysis.

The hydrogen evolved when the solutions were acidified was determined in the following manner: 5 or 10 c.c. of the solution was introduced into a distillation flask of about 75 c.c. capacity, which was fitted with a tap funnel and connected with the Töpler pump. The flask was exhausted, about an equal volume of 20 per cent. sulphuric or hydrochloric acid solution was run into it through the tap funnel, and the hydrogen was pumped off and collected. A measured quantity of N/10 iodine solution was then introduced into the tap funnel, and a small quantity of it was allowed to run into the flask, when a small quantity of hydrogen which was given off was pumped off and collected. The flask was then disconnected from the pump, the remainder of the iodine solution was washed into it, and, after standing for twenty-four hours in a dark cupboard, the excess of iodine solution was determined by means of sodium thiosulphate solution.

We shall refer to the quantity of hydrogen given off when the solutions are acidified, and to the quantity of iodine absorbed by the acid solutions, expressed in gram-equivalents per 100 c.c. of the solutions, as their *hydrogen equivalents* and *iodine equivalents* respectively, and shall represent them in algebraic expressions by the symbols H and I. In chemical formulæ and equations we shall represent the hydrogen which is evolved by the action of acids by the symbol *H* (italic capital), and the hydrogen removed by the action of iodine *in acid solution* by the symbol H (roman capital).

It was usually possible to determine the boron in the com-

pounds, which, besides boron, contained only hydrogen, oxygen, nitrogen, and magnesium, by first heating in a sealed bulb with 1 c.c. of strong nitric acid to oxidize the boron compounds to boric acid. The contents of the bulb was then washed into a platinum crucible containing lime which had been ignited to constant weight. The covered crucible was allowed to stand in an air-bath heated to 120° till the liquid had completely evaporated, and it was then again ignited to constant weight. The increase in the weight of the crucible, less the weight of the magnesium oxide present, if any, gave the weight of the boric acid directly.

To determine the quantity of solid in the solutions, a measured quantity, usually about 10 c.c., was introduced into a hard glass bulb of about 75 c.c. capacity, which was connected with a Töpler pump, and with a receiver which could be immersed either in a freezing mixture or in liquid air. The latter was the more convenient if it was necessary to collect the gas which was given off either from the solution or from the residue. During the distillation the liquid was maintained at about 30°.

In the course of the investigation we had frequently to determine the molecular weights of substances which could only be obtained as salts of magnesium or ammonium in solution. By comparing the properties of the substances under consideration with others which have been more fully investigated, we have been able to apply the necessary correction for the ionization of the salts with a degree of accuracy which we believe to be sufficient for our purpose. In calculating the results we have made use of the following formula, which gives the mean of the number of atoms of boron in the molecule for the substances in the solution:

$$\Delta = 18{\cdot}5\ (\mathrm{B}/n + x\mathrm{Mg} + y\mathrm{NH_4}),$$

where Δ is the depression of the freezing-point;

B is the concentration of the boron in gram-atoms per 100 c.c.;

n is the number of boron atoms in the molecule of the boron compound;

Mg is the concentration of the magnesium in gram-ions per 100 c.c.;

x is the degree of ionization of the compound $(\mathrm{B}_n \ldots)\mathrm{Mg}_m$;

NH_4 is the concentration of the ammonium in gram-ions per 100 c.c.;
y is the degree of ionization of the compound $(B_n \ldots .)(NH_4)_m$.

In the case in which the solutions contained both magnesium and ammonium, usually only a trace of one or the other was present.

PART II

The Two Kinds of Solutions obtained by the Action of Water on Magnesium Boride

Besides the fact that solutions of Class B contain magnesium borate and free boric acid, and consequently yield on warming a copious white precipitate, there is another marked difference between them which must now be referred to. In solutions of Class A, the value of the ratio $I/(H+I)$ lies between 4/9 and 1/2, and as to which is the probable true value will be considered later (p. 25). In the case of solutions of Class B, the value of the ratio approaches 2/3. On treatment of solutions of either class with strong ammonia, the value of the ratio appears to change to 1/3.

Solutions of Class A.

In the preliminary paper the results of some experiments with solutions of this class were described, but further investigations showed that they were probably partly decomposed, and also contained impurities. In the first place we have found that when the solutions are practically free from ammonia, formed by the action of water on magnesium nitride, which is always present in the boride in smaller or larger quantity, they are very unstable, and lose hydrogen rapidly. It was only when the arrangements for excluding the air during the preparation of the boride were imperfect, and magnesium nitride was formed in appreciable quantity, that stable solutions were obtained by treating it with water. We also found that volatile boron compounds, which could be removed by evaporating the solutions *in vacuo*, were present, and that their presence introduced variable errors. Besides this, with experience in dealing with these unstable solutions, we came to understand their character, and arrived at methods of handling them, the details of which cannot be fully described in a paper.

In the preliminary investigation it was assumed that the residue, obtained on evaporating the solutions *in vacuo* and heating the residues, was boric anhydride. This assumption was based upon the fact that the residue, in acid solution, was not oxidized by iodine or by certain other reagents. When, for instance, a solution of it was first treated with dilute nitric acid, and transferred to a crucible containing lime for the determination of the boron, the increase in the weight of the crucible after the water had been driven off at 120°, and the crucible ignited to constant weight, was equal only to the original weight of the residue. It would hardly have been expected that a lower oxide of boron would not become oxidized to B_2O_3 when subjected to such treatment, but this is actually the case.

It appears that the hydrated oxide B_2O_2, which is present in the solution of the residue in combination with a little magnesia, is readily oxidized by air, even in the cold, so long as the solution is nearly neutral. In presence of excess of alkali or acid it is, however, very stable.

To account for the difference between the apparent quantity of boric acid in the original solution and the weight of the boric acid in the residue, we were driven to the assumption that a more volatile form of boric acid existed, and this assumption was supported by the fact that the distillate obtained on evaporating the solutions *in vacuo* always contained boron. Further investigation showed that the loss of boron from the solution on evaporation was insufficient to account for the difference. The residue was then more carefully investigated.

Weighed quantities of the residue were heated for some hours on a water-bath with 1 c.c. of strong nitric acid in a sealed glass bulb. After cooling, the contents of the bulb were washed into a crucible containing lime, for the determination of the boron. The following values were obtained for the ratio:

(Increase in wt. of crucible − MgO) / (Wt. of residue − MgO):

1·25 1·30 1·26 1·21 1·27 1·28 1·24

Assuming that the boron in the residue was completely oxidized to B_2O_3, the above ratio may be expressed as

(Wt. of B_2O_3) / (Wt. of residue − MgO).

Comparing the result with the ratios of the molecular weights of boric anhydride and other possible oxides of boron, we find—

$2B_2O_3/B_4O_5$	1·129
B_2O_3/B_2O_2	1·295
$2B_2O_3/B_4O_3$	1·520

It appears, therefore, that the residue consists of the oxide B_2O_2 with some magnesia.

Boron Dioxide.

We have not been able to isolate pure boron dioxide, which is obtained in solution together with magnesium borite by treating the residue from the borohydrate solution with water, after heating, as we were not able to separate the magnesia from it completely. However, the molecular weight of the compound can be determined in the solution which contains magnesium, on the supposition that the ionization of the borite is of the same order as magnesium sulphate. As a matter of fact, since there appears to be only one atom of magnesium in the solution to three molecules of the oxide, one may neglect the ionization of the borite altogether, without affecting the order of the result. The following are the results of two experiments:

	I.	II.
B	0·0180	0·0132
Mg	0·00305	0·0018
x	0·50	0·50
Δ	0·223°	0·150°
n	1·8	1·8

There are therefore two atoms of boron in the molecule, and the oxide in solution is a hydrate of B_2O_2.

On heating the residue from the borohydrate solution, from which the magnesia has been precipitated with strong ammonia, a residue is left which has the composition corresponding to the formula B_2O_2. It appears, however, to contain traces both of the oxide B_2O_3 and of a compound which is completely insoluble in alkalis and acids, and which may be a lower oxide (*vide* Appendix). The presence of traces of the oxide B_2O_3 vitiates the results obtained for the molecular weights with samples of boron dioxide obtained in this manner.

On evaporation of its solution in air, the oxide B_2O_2 is rapidly oxidized to boric acid, but it appears to be stable in either fairly strong acid or alkaline solutions.

On shaking the solution containing B_2O_2 with some MgO *in vacuo* with light magnesia, obtained by precipitating magnesium nitrate with ammonia, washing the precipitate with ammonia solution, and drying it in desiccator, magnesium passes into solution, the limiting quantity taken up corresponding to a borite of the formula $MgO_2(B_2O_2)NH_2O$. The following are the results of the analysis of a solution which had been in contact with magnesia for a long time:

MgO in 5 c.c.	..	0·0231 gram or 0·00058 gram-molecule.
B_2O_2 ,,	..	0·0611 ,, 0·00113 ,,
Ratio B_2O_2/MgO	..	.. 1·94.

Under the same conditions boric acid forms magnesium metaborate, MgO,B_2O_3.

When the ammoniacal solution of the oxide is evaporated *in vacuo* in the cold, the residue is found to contain only a small and variable quantity of ammonia.

The Relationship between the Sum of the Hydrogen and Iodine Equivalents and the Boron in the Solutions of Class A.

When the boride is prepared in an iron crucible with a closely fitting cover, the solution obtained, on treating it with water, contains 0·0002 gram-equivalent of ammonia per 100 c.c., or even less. The solution obtained on treating the product with water is very unstable, and no constant values can be obtained for the value of the ratio (H+I)/B. The following are some of the values actually obtained:

	I.	II.	III.
H+I	0·0523	0·03985	0·0285
B	0·0226	0·0206	0·0116
(H+I)/B ..	2·31	1·93	2·46

When the boride is prepared in a graphite crucible, it always contains some magnesium nitride, and the solution rarely contains

less than 0·02 equivalent of ammonia per 100 c.c. The following results were obtained with such solutions:

	I.	II.	III.	IV.	V.
H+I ..	0·02135	0·0377	0·0352	0·0175	0·02225
B ..	0·00785	0·0131	0·01075	0·00565	0·0071
(H+I)/B..	2·72	2·88	3·27	3·09	3·13

VI.	VII.	VIII.	IX.
0·04135	0·0538	0·0492	0·07825
0·0151	0·0167	0·0164	0·0244
2·74	3·22	3·00	3·20

The mean value for the ratio (H+I)/B is 3·0, and none of the experimental values depart very far from the mean. It may be pointed out that, if the solution was quite undecomposed, the value should be high, as the boron was determined in the residue obtained by evaporating the solution *in vacuo*. While the hydrogen and iodine equivalents were determined in the original solutions, containing a small quantity of volatile hydroboron.

The Changes which Take Place when the Solutions are Evaporated.

During the evaporation of the solutions *in vacuo* in the cold, only a very small quantity of gas is evolved. As, however, the last trace of moisture disappears (the substances in solution appear to be very soluble), the evolution of the gas from the solid, as it separates, becomes very rapid. The rate of evolution of the gas slackens after the first few minutes, but does not cease altogether for several days, and no end point can be detected.

From the results of our preliminary experiments, it appeared that a connection existed between the hydrogen and the iodine equivalents and the quantities of gas evolved immediately after the liquid had disappeared, on standing, and on heating the residue. A *very large* number of experiments were carried out for the purpose of checking this conclusion, which we do not now consider to have been justified. The results of two experiments

will serve to indicate the nature of the results which were obtained:

	I.	II.
H+I	0·02225	0·0658
Gas evolved after 1 hour	0·0063	—
„ 2 hours	0·0081	0·0233
„ 3 „	0·0088	—
„ 4 „	—	0·02545
„ 6 „	0·01025	—
„ 20 „	0·0109	—
„ 45 „	—	0·03025
„ 111 „	—	0·03185
„ 149 „	—	0·0326

There is possibly some connection between the quantity of hydrogen evolved on long standing and half the value of (H+I), but even this is doubtful. This point must be investigated further.

The quantity of hydrogen evolved on evaporating the solution to dryness and heating the residue is never exactly equivalent to the sum of the hydrogen and iodine equivalents, which may be accounted for by the fact that the distillate always contains volatile boron compounds, and absorbs iodine, and traces of hydrogen are always evolved on treating the residue with acid. Thus:

H+I	**0·02225**	**0·02615**	**0·0175**	**0·01385**
Hydrogen on evaporation and heating	0·02085	0·0230	0·0158	0·01285
Iodine absorbed by distillate	0·0004	0·0008	0·0007	0·0004
Hydrogen from residue	0·0014	0·00325	0·0013	0·0005
Total	**0·02265**	**0·02435**	**0·0178**	**0·01375**

These results are, however, sufficiently concordant to prove beyond doubt that the deviation from exact equivalence between the sum of the hydrogen and iodine equivalents and the hydrogen given off on evaporating the solutions and heating the residues is due only to secondary changes of no importance.

Leaving the magnesia, which is present in these solutions, temporarily out of account, we have now proved that the main product

of the action of heat on the residues obtained on evaporating the solutions is an oxide of the formula B_2O_2. We have also proved that the ratio of the sum of the hydrogen and iodine equivalents (H+I) to the boron in the solutions is 3. If, therefore, the quantity of hydrogen given off on evaporating the solutions and heating the residues is equal to the sum of the hydrogen and iodine equivalents, the simplest formula which represents the mean composition of the substances in the solution may be written H_3BO, to which may possibly be added the elements of water.

The Presence of Magnesium and Ammonium in the Solutions.

The solutions invariably contain magnesium, and it appears that the presence of ammonia, as an accidental impurity, is essential to prevent the substances in solution from decomposing.

The following are the results of some determinations of the boron, magnesium, and ammonium, in certain solutions:

	I.	II.	III.	IV.	V.	VI.	VII.
NH_3 (gm.-mols. per 100 c.c.) ..	0·0310	0·0150	0·0086	0·0049	0·0003	0·0002	0·0002
B (gm.-atoms per 100 c.c.) ..	0·0212	0·0085	0·0156	0·0083	0·0226	0·0206	0·0116
Mg (gm.-atoms per 100 c.c.) ..	0·0030	0·0013	0·0022	0·0012	0·0038	0·0028	0·0022
B/Mg	7·1	6·5	7·1	6·9	6·0	7·3	5·3

The following values of the ratio B/Mg were also obtained in cases in which the ammonia in the solutions was not determined:

5·6 5·45 5·6 6·0 6·0 7·2 6·7 6·5 5·6

The mean value is very nearly 6·0, but the actual values, though they appear to be practically independent of the quantity of ammonia present, for small concentrations, sometimes differ by more than a whole unit from the mean.

If the original solution is made strongly alkaline with ammonia, practically the whole of the magnesia is precipitated; and if

the solution is evaporated nearly to dryness, the residue is found to contain a considerable quantity of combined ammonia. Thus:

	I.	II.	III.	IV.	V.	VI.
B ..	0·0119	0·0161	0·0082	0·00465	0·00715	0·0062
NH_3 ..	0·00375	0·0046	0·0031	0·0015	0·00235	0·00235
B/NH_3	3·2	3·5	2·65	3·1	3·05	2·65

The mean value of the ratio is approximately 3, and it would appear that the magnesium had been replaced by ammonium in equivalent proportion.

On evaporating the ammoniacal solution to dryness *in vacuo* and heating the residue, a substance is left which appears to consist mainly of the oxide B_2O_2. The values for the ratio

(Wt. of B_2O_3 from residue) / (Wt. of residue)

being 1·26, 1·28, 1·32, the value of the ratio B_2O_3 / B_2O_2 being 1·295. On treating the residue with water, a small proportion of it remained undissolved (*vide* Appendix).

The Molecular Weights of the Substances in the Original Solutions of Class A.

Preliminary attempts to determine the molecular weights of the substances in the original solution of Class A from the depression of the freezing-points showed that the results might be vitiated by the presence of volatile impurities. The following method was therefore adopted: A measured quantity of the solution was taken and evaporated almost to dryness *in vacuo* in the cold. About 15 c.c. of pure water was then added, the freezing-point of the solution was measured and compared with that of pure water, and the solution was then analyzed. The following are the results of the experiments:

	I.	II.	III.
B	0·00718	0·00493	0·00360
Mg	0·00124	0·00082	0·00060
Δ	0·090	0·065	0·045
$\left\{x\right.$	0·75	0·75	0·75
$\left.n\right\}$	1·8	1·75	1·8
$\left\{x\right.$	0·5	0·5	0·5
$\left.n\right\}$	1·65	1·55	1·65

Values for n are given corresponding to the extreme values which may be assigned to x on the assumption that the substances in solution behave not dissimilarly to the magnesium salts of acids such as the borite and metaborate, dealt with previously. It must be admitted that many magnesium salts appear to behave abnormally in solution, so far as can be ascertained from the conductivities. However, the following values for the dissociation of 50 litres, which is the mean of the concentrations of the solutions in which the molecular weights were determined, show that there is a certain justification in the selection of these limits.

Salt.	*x at* 50 *Litres.*
Magnesium sulphate	0·6
Magnesium tartarate	0·6
Magnesium citrate	0·55
Magnesium acetate	0·8

The molecular weight (mean) of the substances in the solution in which the magnesium had been replaced by ammonium was determined by the same process. The following are the results of the experiments:

	I.	II.	III.	IV.
B	0·00825	0·00465	0·00715	0·00620
NH_4 ..	0·00170	0·00150	0·00235	0·00235
Δ	0·110°	0·070°	0·105°	0·085°
y	0·75	0·75	0·75	0·75
n	1·8	1·75	1·85	2·2

The concentration of the solutions corresponds to one equivalent in between 40 and 70 litres. At this concentration most ammonium and potassium salts, which behave very similarly, are ionized to the extent of at least 75 per cent. Thus:

Salt.	*y at* 50 *Litres.*
Ammonium chloride	0·92
Ammonium acetate	0·89
Ammonium oxalate	0·82
Ammonium citrate	0·76

If the almost impossibly low value 0·5 is taken for the value of y, the values of n work out at about 0·15 lower than those set

down. It appears, therefore, that the probable value of n is not very far from 2, and that the bulk of the boron compounds in solution probably contain two atoms of boron in the molecule The simplest formula which represents the mean composition of the substances in solution is, therefore, $H_6B_2O_2$, to which may be added the elements of water or magnesia.

The Presence of Water in the Residue obtained on evaporating the Solutions.

From the results of our first experiments, it appeared that the loss of weight on heating the residue was so small that it could be accounted for by supposing that it was due to the evolution of gases, or traces of boric acid, and that the residue contained practically no water. A further series of experiments, conducted with great care, have shown that the loss of weight, though small, cannot be neglected.

A known quantity of the solution was evaporated in a bulb in the usual manner. If the bulb was allowed to remain connected with the pump for an hour or two, the residue came to practically constant weight. It was then heated, and the gas which was evolved was collected, introduced into a density bulb, and weighed. On cooling, the bulb and residue were again weighed. The difference between the loss of weight and the weight of the gas evolved is given in the third line. The following are the results of the experiments:

Solutions containing about 0·02 gram of NH_3 per 100 c.c.

	I.	II.	III.	IV.
B_2O_2	0·0106	0·0041	0·00415	0·0066
MgO	0·0030	0·0013	0·0012	0·00225
Loss (as H_2O) ..	0·0033	0·0022	0·0018	0·0027

Since the gas evolved on heating contained traces of boron compounds, and since a slight sublimate was sometimes observed on heating the residue, it is more than likely that traces of non-gaseous boron compounds were given off and condensed in the pump. In this case the value for the water would be high. It is obvious that it is very difficult, if not impossible, to determine exactly the relationship between the boron dioxide in the residue,

the magnesium, and the water. From the experimental results the relationship may be expressed by

$$B_2O_2 : MgO : H_2O :: 3 : 1 : 1;$$

but it is more probable that the relationship should be represented by

$$B_2O_2 : (MgO + H_2O) :: 2 : 1.$$

In the latter event the solution may contain both $H_6B_2O_2$ and $H_6B_2O_2,H_2O$, the latter as an acid which exists in solution as a magnesium salt somewhat more basic than $(H_7B_2O_3)_2Mg$. The case would be analogous to that of the magnesium phosphates.

The Decomposition of the Substances in the Solutions.

When the liquids are exposed to the air, the value of the hydrogen equivalent falls at about the same rate as when it is contained in an exhausted sealed tube; but the value of the iodine equivalent falls more rapidly than under the latter condition, owing to oxidation.

Since the solutions decompose spontaneously, on standing, the observed values of the sum of the hydrogen and iodine equivalents might be expected to be too low. On the other hand, the presence of traces of volatile hydroborons would tend to raise the observed values. These two sources of error would probably balance one another to a considerable extent.

In determining the relative values of the hydrogen and iodine equivalents, a source of error has to be considered which does not affect the sum of their values. On adding excess of acid to the solutions, the evolution of hydrogen takes place immediately, and the reaction appears to be complete in a few seconds. When, however, iodine solution is added to the acid solution, a further quantity of hydrogen is evolved, equal to from 2 to 4 per cent. of the sum of the equivalents, thus:

$(H+I)$	*Gas evolved on adding Iodine.*
0·0613	0·0017
0·0686	0·0018
0·0347	0·0011

We always collected the gas evolved on adding iodine solution with the hydrogen evolved on adding acid; but whether the figures in the second column above are added to the observed values of the hydrogen or iodine equivalents, the results are affected to an extent which is practically immaterial.

The Relative Values of the Hydrogen and Iodine Equivalents.

Individual experiments show considerable differences in the relative values of the hydrogen and iodine equivalents, but by taking twenty consecutive measurements it is possible to arrive at a fair average. The following are the results of such a series; the figures in the first column indicate that the solution was obtained by the first or subsequent treatment of the boride with water.

	H.	*I.*	*H*+*I.*	*I*/(*H*+*I*)
(1) ..	0·0231	0·0252	0·0483	0·52
(3) ..	0·01615	0·0152	0·03135	0·48
(1) ..	0·0719	0·0682	0·1401	0·49
(2) ..	0·03305	0·0228	0·05585	0·41
(1) ..	0·0308	0·02855	0·05935	0·48
(2) ..	0·0232	0·0188	0·0420	0·45
(3) ..	0·0354	0·0346	0·0700	0·49
(1) ..	0·0410	0·0368	0·0778	0·47
(1) ..	0·0804	0·0540	0·1345	0·41
(2) ..	0·0466	0·0452	0·0918	0·49
(3) ..	0·0419	0·03645	0·07835	0·46
(1) ..	0·0320	0·0145	0·0565	0·43
(2) ..	0·01255	0·0800	0·02055	0·39
(2) ..	0·0355	0·0258	0·0613	0·42
(2) ..	0·0195	0·0179	0·0374	0·48
(1) ..	0·0305	0·0268	0·0573	0·47
(2) ..	0·0288	0·0225	0·0513	0·43
(1) ..	0·04325	0·0320	0·07525	0·43
(1) ..	0·0410	0·0368	0·0778	0·47
(1) ..	0·0804	0·0541	0·1345	0·40
(2) ..	0·0466	0·0452	0·09180	0·49
(3) ..	0·0419	0·03645	0·07935	0·47
(4) ..	0·0290	0·0202	0·0492	0·41
(1) ..	0·0719	0·0682	0·1401	0·49

The mean value of the ratio I/(H + I) from these measurements is 0·455, and the most obvious explanation of this is that the

true value is 0·5, the deviation from it being due to the fact that H and I cannot be determined with any very high degree of accuracy. If this is so, it would appear that the compounds in the solution are either the borohydrate $H_3H_3B_2O_2$ and its hydrates, or an equimolecular mixture of the borohydrates $H_2H_4B_2O_2$ and $H_4H_2B_2O_2$ or of their hydrates. It is, however, possible that the value of I(H+I) is really 4/9 or 0·44, which is very close to the mean of the twenty results set down above. In that case we are driven to the conclusion that the solutions contain the borohydrates $H_2H_4B_2O_2$ and $H_4H_2B_2O_2$, or their hydrates, in the proportion of two molecules of the first to one molecule of the second. Though this is not the *simplest* interpretation to be placed upon the figures, it may be said to be a not impossible one, particularly as the relationship between the boron dioxide and magnesium in the residue, and the water given off on heating, may be represented by

$$B_2O_2 : MgO : H_2O :: 3 : 1 : 1.$$

Evidence of Internal Changes in the Substances in Solution.

The changes which take place when the solutions are allowed to stand in exhausted sealed tubes have already been discussed. Similar experiments were carried out with solutions which had been made strongly alkaline with ammonia, and from which the magnesia had been precipitated. As usual, a large number of experiments were carried out, but they all led to the same conclusion, and it is only necessary to set down the results of two of them:

Time in Days.	*Gas in Tube.*	*H.*	*I.*	*Gas in Tube.*	*H.*	*I.*
0	0·0	0·0344	0·02915	0·0	0·02015	0·01515
1	0·0053	0·0361	0·02295	0·00235	0·0225	0·0115
2	0·0074	0·0345	0·0212	—	—	—
3	—	—	—	0·0037	—	0·0113
4	0·0080	—	0·0217	—	—	—
6	0·0089	0·0348	0·0220	—	—	—
10	0·01115	0·03365	0·0211	0·0050	0·0215	0·0112

These results show that the iodine equivalent falls rapidly till it reaches a value which is almost exactly equal to (H+I)/3, or

0·0206 in the first and 0·0121 in the second series, and then remains practically constant, the value of the hydrogen equivalent *at first rising*, and then falling owing to the decomposition of the substances in solution. It would appear from these experiments that under the influence of strong ammonia internal changes take place which result in the formation of a compound, or compounds, in which the simplest formula representing the relationship of the hydrogen and iodine equivalents is represented by the formula H_4H_2-X.

The Properties of Solutions of Class A.

As the solutions evolved bubbles of hydrogen in contact with all surfaces, and decomposed rapidly in contact with such substances as platinum black, no serious attempt was made to determine their physical properties.

The action of acids and ammonia on the solutions has been fully discussed. Generally speaking, they behave towards organic and inorganic compounds as very powerful reducing agents. They precipitate the heavy metal from the solutions of their salts, but the precipitates contain considerable quantities of boron. With copper salts either a red precipitate of copper hydride, which is soluble in potassium cyanide, or a black precipitate, containing copper and boron, is thrown down, according to the strength of the solutions. Ferric salts are reduced to ferrous salts. An attempt was made to obtain condensation products with aldehydes, ketones, and other organic compounds, but without success.

Solutions of Class B.

When water acts upon magnesium boride which has not " deflagrated " in the process of preparation, or upon the boride prepared in the manner described on p. 7, mixed with 10 per cent. of boric acid, solutions are obtained for which the value of the iodine equivalent is much greater than that of the hydrogen equivalent, and which contain a large quantity of magnesium metaborate and free boric acid in solution. On warming these solutions, magnesium metaborate is thrown down as a thick

precipitate. The following values for the hydrogen and iodine equivalents were obtained for some of the solutions:

	I.	II.	III.	IV.	V.	VI.	VII.
H	0·0072	0·0248	0·01905	0·0108	0·02235	0·03595	0·02235
I	0·0123	0·0412	0·03235	0·0183	0·0406	0·0626	0·04060
H/I	0·59	0·58	0·59	0·59	0·55	0·57	0·55
I/(H+I)	0·63	0·62	0·63	0·63	0·64	0·63	0·64

The value of the ratio H/I is always greater than 1/2, but it appears probable that this is the true value, since changes which take place spontaneously in the solutions tend to make the value of the ratio too great. The decomposition of the solutions was investigated in a manner identical to that employed in the solutions of Class A, measured quantities being placed in exhausted sealed tubes, and examined after standing at constant temperature. The results of a single experiment will serve to indicate the nature of the results:

Time in Hours.	*H.*	*I.*	*Gas in Tube.*
0	0·01905	0·03235	0·000
24	0·01875	0·02995	0·00195
48	0·01885	0·0294	0·0024

It will be seen that the value of the iodine equivalent decreases more rapidly than that of the hydrogen equivalent, which would tend to raise the value of the ratio H/I.

It would appear, therefore, that the formula which represents the mean composition of the substances present in solutions of Class B may be written $H_2H_4 - X$.

When ammonia was added to the solutions, magnesium metaborate was thrown down, and changes took place which are of great interest, but which, unfortunately, it has not been found possible to follow with a very great degree of accuracy. A solution of Class B was taken, and, after determining the constants,

it was mixed with an equal volume of 50 per cent. ammonia solution, and the constants were again determined. The following results were obtained:

	Original Solution.	*Ammoniacal Solution.*
H	0·00980	0·01175
I	0·01705	0·01555
H/I	0·57	0·75

The original solution was allowed to stand for twenty-four hours, and the experiment was repeated:

	Original Solution (after 24 Hours).	*Ammoniacal Solution.*
H	0·00935	0·01340
I	0·01595	0·00910
H/I	0·58	1·47

If the ammoniacal solution was warmed, the change proceeded more rapidly, but was accompanied by the decomposition of the substances in the solution. Thus:

	Original Solution.	*Ammoniacal Solution after Warming.*
H	0·00985	0·0131
I	0·01445	0·00825
H/I	0·67	1·59

Again, on evaporating the solution to small bulk, after adding ammonia, the change appeared to become more complete; but, as some hydrogen was given off during evaporation, the value of the hydrogen equivalent which includes this quantity of hydrogen is probably somewhat too high. Thus:

	Original Solutions.		*Ammoniacal Solutions after Evaporation.*	
	I.	II.	I.	II.
H ..	0·00720	0·00750	0·01260	0·01275
I ..	0·0123	0·01160	0·00600	0·00415

It would appear from these results that the changes which take place in these solutions, and which are hastened by the action of

ammonia, and by the increase of temperature, may be generally represented by the equation

$$H_2H_4-X \longrightarrow H_4H_2-X.$$

This conclusion may certainly be regarded as somewhat speculative, but it is supported by the fact that similar changes take place in solutions of Class A under similar conditions.

On evaporating the solutions to dryness and heating the residues, hydrogen was given off, the quantity of which was almost exactly equivalent to the sum of the hydrogen and iodine equivalents. Thus:

	I.	II.
H+I	0·01690	0·02630
Hydrogen on heating ..	0·01760	0·02480

The quantity of boron and magnesium in the solutions was determined in a number of cases and compared with the value of the hydrogen and iodine equivalents, and it was found that the values were lowest in the case of solutions obtained by treating a mixture of magnesium boride and boric acid with water. Solutions prepared by treating the boride, which had not been sufficiently heated, with water contained large excess of magnesium borate. The following are some analyses of solutions prepared by the former method:

	I.	II.	III.
H	0·0287	0·0248	0·02235
I	0·0477	0·04155	0·0406
(H+I)	0·07645	0·06635	0·06295
B	0·0445	0·0481	0·0415
Mg	0·0113	0·0112	0·0104
(H+I)/B/Mg ..	1·7/1/0·25	1·6/1/0·25	1·5/1/0·25

These results, which appear very concordant, seem to lead to the conclusion that the mean composition of the substances in solution may be represented by the formula H_6B_4Mg. However, on warming the solutions, or on adding ammonia to them, they deposit varying amounts of magnesium borate, and it is obvious that they always contain this substance in considerable quantity. How to get rid of the excess of magnesia and boric acid was the next problem which we had to face, and it was not by any means

a simple one to solve, since no chemical method appeared to be available.

In the course of experiments on magnesium metaborate, which have been referred to earlier in this paper, it had been observed that when light magnesia was shaken with a solution of boric acid a solution was at first formed containing a metaborate of the formula $B_2O_3(MgO)$. If large excess of magnesia were present, and the solution were shaken for a long time, the magnesium metaborate, which is only slightly soluble in water, but which forms supersaturated solutions, separated out. By this means it appeared possible to separate boric acid almost completely from solution, a solution of the metaborate which had been so treated being found, on analysis, to contain only 0·0024 gram-atom of boron per 100 c.c.

In the first experiment, four separate quantities of a solution were taken. One of them was analyzed immediately, and the other three were sealed up in exhausted tubes with some light magnesia, and examined after shaking for 24, 48, and 96 hours. The following results were obtained:

Time.	*H.*	*I.*	*Gas in Tube.*	*B.*	*Mg.*
0	0·01905	0·03235	0·00	0·144	0·023
24	0·01875	0·02995	0·00195	0·0195	0·0046
48	0·01855	0·02965	0·0024	0·0228	0·0049
96	—	—	—	0·0212	0·0050

It will be observed that the boron and magnesium content is least in the case of the solution which has been shaken for the shortest time, but that the limit reached in all three cases is practically the same. How much magnesium borate remains in solution is, of course, impossible to determine; but as the solution, after shaking with magnesia, still contains magnesium ions and since magnesium metaborate is very insoluble, the quantity of it which remains behind is certainly very small, the boron corresponding to it being probably less than 0·0024 gram-atoms of boron per 100 c.c., the value obtained by shaking boric acid with magnesia in the absence of other magnesium salts.

The original value of the sum of the hydrogen and iodine equivalents, and the minimum values for the boron and magnesium concentrations, give us the ratio

$$(H+I) : B : Mg :: 2{\cdot}6 : 1 : 0{\cdot}23.$$

The second experiment was carried out similarly, and the following results were obtained:

Time.	*H.*	*I.*	*Gas in Tube.*	*B.*	*Mg.*
0	0·0108	0·0183	0·0	—	—
48	—	—	0·00245	0·00995	0·0030
112	0·01275	0·01375	0·00295	0·0099	0·0030

(H+I) : B : Mg :: 2·9 : 1 : 0·3.

In this case again the boron fell to a minimum in two days.

In the third experiment a considerable quantity of the solution was shaken with light magnesia, and after two days it was filtered and divided into two portions. One portion (*a*) was analyzed, and the other (*b*) was shaken for a further period of two days with fresh magnesia. The following results were obtained:

Time.	*H.*	*I.*	*Gas in Tube.*	*B.*	*Mg.*
0	0·03595	0·0620	0·00	0·054	0·0128
(*a*) 48	0·0340	0·0508	0·0087	0·038	0·0074
(*b*) 112	0·0354	0·04725	0·0117	0·033	0·0067

(*a*) (H+I) : B : Mg :: 2·5 : 1 : 0·2.
(*b*) (H+I) : B : Mg :: 2·9 : 1 : 0·2.

These results give us the maximum quantities of boron and magnesium which are present other than as magnesium metaborate. It appears likely, therefore, that the value for the ratio (H+I) : B : Mg must approach the value 3 : 1 : 0·3, which is identical for that found for solutions of Class A.

Magnesium metaborate is a hydrated salt, and hence, when the solutions of Class B were evaporated to dryness, the residues, which contained traces of it, also contained moisture, and it was found impossible to obtain accurate results for the determination of the relationship between the weight of the residue and the boric acid derived from it. Further experiments might have led to a solution of the difficulties which were encountered, but at this stage the investigation had to be brought to an end. However, it may fairly be assumed that the residue, as in the case of solutions of Class A, must consist of the oxide B_2O_2 with some magnesia.

Leaving water and magnesia out of account, the mean composition of the compounds in the solutions of Class B may then

be represented by the formula $H_2H_4B_2O_2$, to which may be added the elements of water, and it appears that under certain conditions a change takes place which may be represented by the equation

$$H_2H_4B_2O_2 \longrightarrow H_4H_2B_2O_2.$$

It will be observed that a similar change takes place in solutions of Class A.

Summary of the Results arrived at in Parts I. and II.

1. The action of water upon magnesium boride may be represented by the equation

$$Mg_3B_2 + 6H_2O = 3H_2 + Mg_3B_2(OH)_6.$$

The main product of the reaction, which is completely insoluble in water, may be regarded as a compound of magnesia with a borohydrate of the formula $B_m(OH_2)_n$.

2. As a result of secondary reactions, gaseous compounds of boron and hydrogen (hydroborons), and soluble solid compounds of boron, hydrogen, and oxygen (borohydrates), are also formed. On the addition of acids to the solutions of the borohydrates hydrogen is evolved, and the acid solutions decolorize iodine.

3. The properties of the solutions obtained from magnesium boride which is free from boric acid (Class A) differ from those obtained from the boride which contains boric acid (Class B).

4. On evaporating the solutions of Class A to dryness and heating the residue a mixture of the oxide B_2O_2 with magnesia is obtained. This oxide has been investigated.

5. The solutions are very unstable, but their stability is increased if traces of ammonia are present.

6. Analyses and molecular weight determinations indicate that the mean composition of the substances in solutions of Class A, leaving water, ammonia, and magnesia, out of account, is represented by the formula $H_6B_2O_2$.

7. The magnesia content of solutions of Class A, and of solutions of Class B which have been freed from magnesium borate,

is represented by the formula $3H_6B_2O_2,MgO$. The ammonia content is variable, but negligible. Analytical methods have failed to give any sure indication of the quantity of water in combination with the boron, but the quantity is certainly small. From actual analytical results, it appears that the composition of the residues obtained by evaporating the solutions (Class A) *in vacuo* in the cold may be represented by $3H_6B_2O_2$, $2(MgO,H_2O. \ . \ .)$ or $2H_6B_2O_2,(MgO,H_2O. \ . \ .)$. The solutions may contain compounds of the formulæ $H_6B_2O_2$ and $H_6B_2O_2,H_2O$, partly in combination with magnesia.

8. Experimental determinations of the relative values of the hydrogen and iodine equivalents lead to the conclusion that the main composition of the compounds in solutions of Class A may be represented by the formula H_3H_3-X, but that it is more probable that these solutions contain a mixture of compounds represented by the formulæ H_2H_4-X and H_4H_2-X. On allowing a solution of Class A to stand with strong ammonia a change takes place which may be represented by the equation

$$H_2H_4-X \longrightarrow H_4H_2-X.$$

9. Solutions of Class B appear to contain a compound or compounds the mean composition of which may be represented by H_2H_4-X, probably $H_2H_4B_2O_2$ or $H_2H_4B_2O_2,H_2O$, combined with some magnesia. Under certain conditions a change similar to that indicated in the last paragraph takes place in the solutions.

Conclusion to Part II.

The results of these experiments point to the existence of isomeric substances of the formula $H_6B_2O_2$ or $H_6B_2O_2,H_2O$, which are present in the original solutions, at least partly, as magnesium salts. Using the symbolism which we have adopted, the possible isomers may be represented by—

(*a*) $H_3H_3B_2O_2$	(*a'*) $H_3H_3B_2O_2,H_2O$.
(*b*) $H_2H_4B_2O_2$	(*b'*) $H_2H_4B_2O_2,H_2O$.
(*c*) $H_4H_2B_2O_2$	(*c'*) $H_4H_2B_2O_2,H_2O$.

Though the analyses of the solutions of Class A make it appear that the mean composition of the solutions is fully represented by formulæ (*aa'*), it seems to be much more likely that these solutions contain a mixture of the substances represented by (*bb'*) and (*cc'*). On treating these solutions with ammonia, a change takes place which may be represented by,—

$$H_2H_4 - X \longrightarrow H_4H_2 - X.$$

Solutions of Class B contain mainly a compound, or compounds, of the formula H_2H_4–X(*bb'*), which readily change into compounds of the type $H_2H_2 - X(cc')$. Hence the assumption that compounds of the type $H_3H_3 - X(aa')$, the simplest formula which could be assigned to the compounds in solutions of Class A, exist at all, only complicates matters. We shall see later that the simultaneous elimination of three atoms of hydrogen from such a compound is most unlikely to happen.

Since compounds of the type $H_6B_2O_2$ and $H_6B_2O_2,H_2O$, and the products which are formed from them by the elimination of hydrogen, are not distantly related to nitramide and hyponitrous acid, it is not surprising that they exhibit isomerism, and we shall now proceed to show how the different isomerides may be constituted.

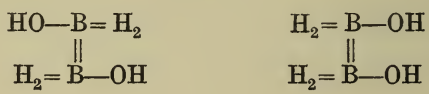
A study of recent investigations on the boron compounds leads to the conclusion that, except in a few unimportant cases in which the composition of the compounds is doubtful, it is possible to assign formulæ to the compounds on the assumption that boron is always trivalent or pentavalent. The hydroborons B_2H_6 and B_4H_{10} may, for instance, be written: $BH_3 = BH_3$, $BH_3 = BH_2 - BH_2 = BH_3$. The formula which we assign to the hydroboron B_4H_{10} finds support in the results of the experiments recorded in Part III. of this paper.

Since under certain conditions the compound $H_6B_2O_2$ loses four atoms of hydrogen, and is probably converted into a compound $H_2B_2O_2$, it is obvious that the relationship of the borohydrates which we have investigated and the compounds hyponitrous acid and nitramide is a very close one. Unfortunately, the relationship between the two latter compounds is still a matter for speculation, but it is possible that researches on the boron

compounds may throw some light on the constitution of the related nitrogen compounds.

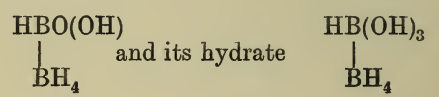
It has been suggested that the nitrogen compounds are stereo-isomerides, and may be represented thus:

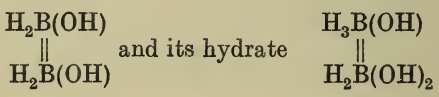
Similarly, we might represent the boron compounds by—



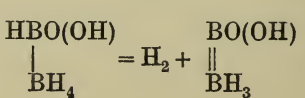
and it will be observed that the symmetrical form, which would probably be the most stable, would have four atoms of hydrogen in adjacent positions. This might account for the fact that the more stable form is the one which loses four atoms of hydrogen in presence of acid.

However, this solution would not help us to explain the facts recorded in Part III. of this paper, and we are of opinion that, as in the case of the nitrogen compounds, the existence of isomers may be accounted for and explained by simple structural formulæ. We may represent them thus:





The existence of intermediate forms is possible in the case of the compound $H_6B_2O_2$, but not of its hydrate. The first formula represents the unstable form $H_2H_4B_2O_2$, or its hydrate, which loses one molecule of hydrogen readily thus:



The second formula represents the stable form $H_4H_2B_2O_2$, or its hydrate, which loses four atoms of hydrogen thus:

$$\begin{matrix} H_2B(OH) \\ \| \\ H_2B(OH) \end{matrix} = 2H_2 + \begin{matrix} B(OH) \\ \| \\ B(OH) \end{matrix}$$

We do not find it possible to write the formula for a compound represented by $H_3H_3B_2O_2$, which would readily lose three atoms of hydrogen.

We have not lost sight of the fact that it is possible that, while the compound $H_6B_2O_2$ may represent the stable form, its hydrate $H_6B_2O_2,H_2O$ may represent the stable form, or *vice versa*. We do not, however, look upon this as a probable explanation of the results of our experiments.

PART III

Action of Ammonia on Magnesium Boride after Treatment with Water.

With the object of isolating the borohydrate $B_m(OH_2)_n$ as an ammonium salt, a quantity of the " spent " boride, obtained by the prolonged treatment of the crude boride with water (p. 10), was treated with strong ammonia solution in an atmosphere of hydrogen. At first a small quantity of hydrogen was evolved; but on treating the spent boride with successive quantities of ammonia solution, though the reaction resulting in the formation of the borohydrate, which we shall now describe, proceeded with undiminished rapidity, the rate of evolution of the hydrogen slackened, and finally ceased altogether. It appears, therefore, that the reaction which gives rise to this borohydrate takes place without the evolution of hydrogen; and since, as was pointed out on p. 10, the reaction between the original boride and water comes to an end only with extreme slowness, it is probable that the hydrogen which is evolved on first treating the spent boride with ammonia is due to the presence in it of traces of undecomposed boride. It was noticed that, however long the ammonia solution was allowed to stand in contact with the spent boride, the concentration of the borohydrate in it never rose beyond a certain limiting value.

The solution obtained in this manner contained a borohydrate which appeared to be very fairly stable in presence of excess of ammonia, as it did not lose hydrogen when the solution was preserved in an exhausted sealed tube, or suffer oxidation when the ammoniacal solution was exposed to the air. On addition of acids, hydrogen was evolved with brisk effervescence, and the acid solution absorbed iodine. The solution contained a

trace of magnesium. On evaporation to dryness *in vacuo* in the cold, a white crystalline residue was left, which contained, besides boron, hydrogen, and oxygen, the elements of ammonia, and which evolved hydrogen slowly on standing. On heating, hydrogen was given off, and a residue was left, which, as we shall show, appears to be the oxide B_4O_5.

The hydrogen and iodine equivalents, the magnesium in the original solution, the boron in the residue obtained by evaporating the solution to dryness, and the ammonia evolved by the action of alkali on the solution which had been evaporated to small bulk in the cold, were determined in the manner already described. The following are the results of the experiments, which are, as usual, expressed in gram-atoms or gram-molecules per 100 c.c. of the original solution:

H equiv.	0·0075	0·0090	0·0069	0·0060	0·0077
I equiv. ..	0·0035	0·0042	0·0032	0·0028	0·0037
NH_3 ..	0·0034	0·0037	0·0029	0·0028	0·0033
B ..	0·0068	0·0080	0·0064	0·0056	0·0072
Mg ..	0·0003	0·0004	0·0002	0·0001	0·0001

The results show that the following relationships hold good:

$$\text{H equiv.} : \text{I equiv.} : (NH_3 + Mg) : B :: 2 : 1 : 1 : 2.$$

As in the former experiments, the nature of the residue was carefully investigated; and as the results obtained in these experiments differed considerably from those obtained in the former, seven separate determinations of the value of the ratio,

$$(B_2O_3 \text{ in residue}) / (\text{Weight of residue less MgO})$$

were made, and the following values for it were obtained:

1·13 1·18 1·12 1·10 1·13 1·15 1·14.

When the residue consists of the oxide B_2O_2, the value of the ratio is 1·295. In the case of the residue obtained in the present experiments, the value approximates very closely to 1·129, which is the value of the ratio B_2O_3/B_4O_5.

The Oxide B_4O_5.

It is convenient at this stage to consider our attempts to obtain a pure solution of this oxide, and to determine its molecular weight. When the oxide was allowed to remain in contact with water in an exhausted bulb, it dissolved almost completely, leaving a small amount of residue (*vide* Appendix), which was insoluble in acids. The solution was golden-yellow in colour.

The freezing-points of the solutions were determined in the manner already described, and were compared with the freezing-point of pure water, and from the depression of the freezing-point and the concentrations of the boron and magnesium, which were obtained by the analysis of the solutions, the value of n, the number of atoms of boron in the molecule of the oxide, was calculated. The following are the results of the experiments:

	I.	II.	III.
B	0·0190	0·0102	0·0129
Mg	0·0009	0·0003	0·0008
Δ	0·169	0·082	0·110
n	2·31	2·51	2·43

The results of the analyses of the residue leave no room for doubt as to its composition, which corresponds to the formula B_4O_5. However, it is very easily oxidized, and when a solution of it is allowed to remain for a few hours in contact with air, nothing but boric acid remains. Since the oxidation takes place in accordance with the equation

$$2B_4O_5 + O_2 + 12H_2O = 8B(OH)_3,$$

for every molecule of the higher oxide decomposed four molecules of boric acid are produced. The influence of the latter compound in lowering the mean moleculer weight of the substances in the solution makes it very difficult to determine the true molecular weight of the oxide B_4O_5.

We first attempted to separate the oxides in the solution by shaking the solution with light magnesia, a method which has already (p. 31) been employed for the elimination of boric acid. After shaking a quantity of the solution for two days with light

magnesia, a determination of the depression of the freezing-point of the solution showed that it contained only magnesium metaborate, the ratio B/Mg being almost exactly 2, and the value of n only just above unity. The oxide B_4O_5 had either been decomposed, or removed from the solution in combination with the magnesia.

We next attempted to separate the constituents of the solution by fractional crystallization. A quantity of the solution was evaporated to small bulk *in vacuo* in the cold, and the concentrated solution was cooled for an hour in an ice-bath. The crystals which formed were separated by filtration, and both liquid and crystals were made up to 15 c.c. with water. The following results were obtained from the examination of the solutions:

	Liquid.	*Crystals.*
B	0·0285	0·00735
Mg	0·0009	0·0002
Δ	0·205	0·085
n	2·79	1·67

By this process a slight increase in the concentration of the substance of higher molecular weight had been effected, but as it was the more soluble of the two substances which appeared to be present, on account of its unstable character, and of the fact that the impurity of lower molecular weight was being formed from it continuously, it did not seem possible to purify it completely. It remained, however, to prove that the compound of lower molecular weight was boric acid. A quantity of the solution was therefore evaporated as before, and the crystals were filtered off and recrystallized from water. The following results were obtained:

B	0·00405
Mg	0·00005
Δ	0·079
n	0·94

This result leaves no doubt that this substance is boric acid.

If we accept the fact that the composition of the residue

corresponds with the formula B_4O_5, we must assume that it consists of—

(*a*) The oxide B_4O_5 with traces of the oxide B_2O_3.
(*b*) A mixture of the oxides B_2O_2 and B_2O_3.
(*c*) A " B_3 " oxide, together with B_2O_3.

The mixture of composition (*b*) would have a mean molecular weight very little above unity, and consequently much lower than that obtained for the residue in solution. If the residue contained a " B_3 " oxide, then that substance must have been obtained practically free from boric acid by the single fractionation referred to above. We are therefore brought back to the conclusion that the oxide in solution, as in the solid state, has the composition represented by the formula B_4O_5, but that it is impossible to separate it from the boric acid, of which it originally contains traces, and which is formed from it by oxidation.

Decomposition of the " B_4" Borohydrate.

We have now to consider the action of heat on the residue obtained by evaporating the original solutions. In the case of the borohydrates already described, the quantity of hydrogen evolved is exactly equal to the sum of the hydrogen and iodine equivalents; but in the case of the borohydrate which we are describing, hydrogen is evolved on heating, which is not removed either by the action of acid or of iodine. The operation was performed in the manner already described, but it was observed that it was necessary to heat the residue very nearly to the softening-point of hard glass before the last trace of hydrogen was evolved.

The following are the results of our experiments:

	I.	II.	III.
H equiv. I equiv.	0·0073	0·00575	0·0072
Gas on heating	0·0135	0·01015	0·0129
Ratio	6/11·1	6/10·4	6/10·8

The experimental values of the ratio cannot be determined so accurately as to enable us to decide whether its true value is 6/10 or 6/12. In this respect we are face to face with a difficulty which is met with every day in dealing with the composition of organic compounds, and, following the procedure of the organic

chemist, we can arrive at a decision as to which value to accept from the following considerations. As we shall presently see, if we adopt the value 6/10, we shall be able to explain the following facts:

(*a*) That the borohydrate is formed from the spent boride without the evolution of hydrogen, and without change in composition in that portion of the spent boride which is not converted into soluble borohydrate.

(*b*) That only two atoms of hydrogen are removed from the borohydrate by the action of iodine in acid solutions.

The Molecular Weight of the Borohydrate.

The molecular weight of the borohydrate in the solution was determined in the manner already described, the ammoniacal solution being evaporated to small bulk to remove the excess of ammonia, and the solution made up to 20 c.c. for the experiment. The boron, ammonia, and magnesium, in the solution were afterwards determined. The following are the results of the experiments:

	I.	II.	III.
B	0·0064	0·0056	0·0072
NH_3	0·0029	0·0026	0·0033
Mg	0·0002	0·0001	0·0003
Δ	0·085°	0·075°	0·095°

We are here dealing with the ammonium salt of a fairly strong acid, which does not evolve ammonia to any extent when the solution is evaporated. It is probable that the degree of ionization of the salt will be closely comparable with that of ammonium oxalate, and, as ammonium and potassium salts behave very similarly, we may, for the sake of comparison, make use of the values of the degree of ionization for potassium oxalate which have been published by Noyes and Johnston (*J. Am. Chem. Soc.*, **31**, 1001). According to these authors, at a concentration of 0·03 equivalent per litre, potassium oxalate is between 80 and 85 per cent. dissociated; and applying these values to the calculation of the numbers of atoms of boron in the molecule of the borohydrate, we obtain the following results:

	I.	II.	III.
85 per cent. dissociated ..	3·3	3·25	3·6
80 „ „	3·1	2·95	3·35

From these results, taken by themselves, it would appear that there are three or four atoms of boron in the molecule. It is, however, quite impossible to reconcile the former result with those obtained from the study of the chemical properties of the borohydrate, particularly the fact that for every two atoms of boron—

1 equivalent of ammonia is removed on warming with alkali;
2 atoms of hydrogen are evolved on adding acid to the solution;
1 atom of hydrogen is removed by treating the acid solution with iodine.

The results are too concordant to admit of any other conclusion but that the number of atoms of boron in the molecule is some multiple of 2. If there are only two atoms of boron in the molecule, and no impurity of higher molecular weight is present, the salt can only be 45 per cent. dissociated, a condition which is altogether improbable. On the other hand, if any impurity is present, it is likely to be of low molecular weight; and considering the unstable character of the borohydrates, it is not at all unlikely that even such treatment as the evaporation of the solution may give rise to the presence of decomposition products of lower molecular weight than the original substance. We may therefore conclude that the borohydrate which is under discussion contains four atoms of boron in the molecule.

We have therefore very good reason for concluding that the compound in solution has the formula $H_{12}B_4O_6,2NH_3$.

The Constitution of the Borohydrate.

If we again make the simple assumption that the evolution of hydrogen on addition of acids to the solution involves the removal of pairs of hydrogen atoms from adjacent boron atoms, and give to the compound the simplest possible formula, representing the boron atoms as forming a chain, with the hydrogen and hydroxyl groups arranged symmetrically with regard to them, we can easily account for the reactions which have been described.

On treating the original solution with acid, leaving the ammonia out of account, a reaction takes place which may be represented by—

$$BH_2(OH)_2 \cdot BH(OH) : BH(OH) \cdot BH_2(OH)_2$$
$$= 2H_2 + BH(OH)_2 : B(OH) \cdot B(OH) : BH(OH)_2.$$

On treating the acid solution with iodine, the remaining two hydrogen atoms, which are connected directly to the boron atoms, will be removed, forming a compound of the formula

$$B(OH)_2 \cdot B(OH) \cdot B(OH) \cdot B(OH)_2.$$

On heating the residue obtained by evaporating the original solution *in vacuo*:

$$BH_2(OH)_2 \cdot BH(OH) : BH(OH) \cdot BH_2(OH)_2(+2NH_3)$$
$$= 5H_2 + BO : BO \cdot BO : BO\,(+2NH_3).$$
$$\underline{\quad\quad O\quad\quad}$$

It may now be pointed out that if, on heating, the quantity of hydrogen evolved is equivalent to six, and not to five molecules, it will be necessary to give the original borohydrate the formula

$$BH_2(OH)_2 \cdot BH_2(OH) \cdot BH_2(OH) \cdot BH_2(OH)_2.$$

On treating the solution with acid, one molecule of the borohydrate would almost certainly lose four molecules of hydrogen, four pairs of hydrogen atoms being removed from adjacent boron atoms. This is an additional argument in favour of the acceptance of the lower value for the hydrogen given off on heating.

APPENDIX

When ammoniacal solutions either of the B_2 or B_4 borohydrates were evaporated, the residues, after heating, were almost completely soluble in water, but left a slight residue which was insoluble both in acids and alkalis (pp. 16, 40). The residue was light brown in colour. On heating it gave off both water and hydrogen, the latter being apparently derived from combined water by decomposition. The quantity obtainable from any single experiment was very small, but by collecting the residues from two series of experiments, two quantities of 0·08 and 0·03 gram were obtained for analysis. The following results were obtained:

1 gram of compound contains 0·0377 boron and 0·0266 water.
1 „ „ „ 0·0394 „ 0·0290 „

The compound does not appear to contain nitrogen, though it may be derived from a nitride by the action of water. It appears to be a hydrated derivative of an oxide lower than those already described, and possibly the oxide B_2O. Its presence, or the presence of the corresponding nitrogen derivative, in the residues from the ammoniacal solutions of the borohydrates explains the presence of boric acid in these residues.

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